

AD-A117 680

NEW YORK UNIV NY DEPT OF CHEMISTRY

F/6 20/8

ANOMALOUS REORGANIZATION FREE ENERGIES IN OPTICAL ELECTRON TRAN--ETC(U)

JUN 82 P DELAHAY

UNCLASSIFIED

TR-1

NL

1-1

1-1

1-1

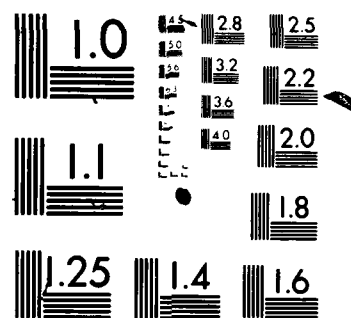
END

DATA

FILED

68-82

DTIC



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

AD A117080

6  
12

OFFICE OF NAVAL RESEARCH

Contract N00014-82-K-0113

Task No. NR 359-258

TECHNICAL REPORT NO. 1 (New Series II)

ANOMALOUS REORGANIZATION FREE ENERGIES  
IN OPTICAL ELECTRON TRANSFER IN SOLUTION

by

Paul Delahay

Accepted for publication in  
Chemical Physics Letters

New York University  
Department of Chemistry  
New York, NY

June 1982

DTIC FILE COPY

DTIC  
JUL 26 1982  
E

Reproduction in whole or in part is permitted for  
any purpose of the United States Government

This document has been approved for public release  
and sale; its distribution is unlimited

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

DD FORM 1 JAN 73 1473

Unclassified

**SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)**

# ANOMALOUS REORGANIZATION FREE ENERGIES IN OPTICAL ELECTRON TRANSFER IN SOLUTION

PAUL DELAHAY

Department of Chemistry, New York University, New York, New York 10003

Autoionization bands are observed in the photoelectron emission spectroscopy of aqueous solutions of cyanometalate complexes (Mn, Fe, W, Mo), anions ( $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ) and cations ( $\text{Ag}^+$ ,  $\text{Tl}^+$ ). Reorganization free energies for autoionization bands are anomalously low in absolute value (by ca. 1 eV) in comparison with direct transitions to the continuum. Interpretation is based on potential energy profiles and model calculations for the reorganization free energy.

Solutions of certain ions (e.g.,  $\text{Fe}(\text{CN})_6^{4-}$ ) in various solvents exhibit two distinct bands for emission of photoelectrons in the solvent vapor above the solution. The emission bands consist of a plot of the emission yield (number of collected electrons per incident photon) against photon energy. The first band is observed at photon energies lower by ca. 1 eV than expected from the energetics of electron emission and subsequent reorganization of nuclear configurations. Conversely, the second band is observed in the expected range of photon energies. These results will be interpreted in the present paper by considering emission by autoionization and direct transition to the continuum.

## 1. Autoionization in solution

Photoelectron emission by solutions will be interpreted on the basis of potential energy profiles similar to those used in the discussion of thermal electron transfer [1,2]. The species being photoionized and the resulting product are denoted, respectively, by  $\text{D}^-$  and D regardless of actual ionic



charges (to simplify notations). The curve  $U(D^-)$  in Fig. 1 (left) represents the variations of the potential energy of the solvated species  $D^-$  with a generalized coordinate depending on the nuclear configuration of  $D^-$  and the solvent. The reduction of potential energy hypersurfaces to a two-dimensional representation is discussed in [1,2]. Curve  $U(D, e^-)$  pertains to the products of photoionization, namely  $D$  and the electron in the gas phase. The constant potential energy of the electron at infinity in the gas phase is included in  $U(D, e^-)$ . The minimum of the  $U(D^-)$  curve corresponds to the ground state of  $D^-$ . Conversely, the minimum of the  $U(D, e^-)$  curve pertains to the ground state of  $D$  and the electron at infinity in the gas phase (treated as a vacuum). The two minima are separated by the energy gap  $U_C$ .

Photoelectron emission into the gas phase results from the vertical transition AB (Franck-Condon principle) involving the difference in potential energy  $U_{AB} = U_C - U_r$ , where  $U_r$  ( $< 0$ ) is the energy for reorganization of the solvated species produced by photoionization. The reorganization process is represented by the segment BC of the  $U(D, e^-)$  curve. The kinetic energy of the electron emitted into the gas phase depends on  $U_{AB}$  and the photon energy.

Suppose that the excited state  $D_{ex}^-$  is prepared by the transition AE requiring the change in potential energy  $U_{AE}$  (Fig. 1, right). This transition satisfies the condition  $U_C < U_{AE} < U_C - U_r$ . In that case, radiationless transitions may occur between the discrete levels of  $D_{ex}^-$  and continuum levels of  $(D, e^-)$ , and autoionization may occur [3]. The discrete-continuum interaction can be interpreted as the result of the intersection [1,2] of the potential energy curves of  $D_{ex}^-$  and  $(D, e^-)$  (Fig. 1, right). If there is autoionization, photoelectron emission into the gas phase is observed for a change of potential energy  $U_{AE}$  lower than  $U_{AB} = U_C - U_r$ . Two distinct emission bands are observed if  $U_{AB}$  and  $U_{AE}$  differ sufficiently. Moreover, the reorganization

energy  $U_r' = U_c - U_{AE}$  for the autoionization band is lower in absolute value than  $U_r = U_c - U_{AB}$  for the band for direct transition to the continuum.

Interaction between discrete and continuum levels considered in the preceding discussion was already invoked in the interpretation of the emission bands of anthracene mono- and divalent anion radicals in solution [4]. Autoionization was inferred in that work from the near coincidence of emission and absorption bands. The interpretation was not cast in terms of potential energy profiles, and the reorganization process was not considered. The main points of the present paper therefore did not appear in [4].

## 2. Anomalous reorganization free energies

Autoionization is detected in this work from the anomalously low absolute value of the reorganization free energy  $R$ . Basic equations and methods for the analysis of data were recently reviewed [5]. The value of  $R$  is computed from [1,6]

$$\Delta G^m = \Delta G_H + \Delta G - R, \quad (1)$$

where  $\Delta G^m$  is the free energy for emission;  $\Delta G_H = 4.50$  eV on the assumption of a negligible ( $\pm 0.1$  V) surface potential at the solution-water vapor interface;  $\Delta G$  is the free energy change for the reaction,  $D^-(aq) + H^+(aq) = D(aq) + 1/2H_2(g)$ . The sum  $\Delta G_H + \Delta G$  in (1) corresponds to the change of potential energy  $U_c$  in sec. 1. One sets  $\Delta G^m = E^t$ , where  $E^t$  is the experimentally determined threshold energy. This equality holds within ca.  $\pm 0.2$  eV or better [7]. The quantity  $E^t$  is obtained from a linear plot of  $Y^n$  vs.  $E$ , where  $Y$  is the emission yield,  $E$  the photon energy, and  $n = 0.4$  or  $0.5$ . The extrapolation method is discussed in [5].

Anomalously low values of  $|R|$  computed from (1) can be identified by comparison with the results of model calculations [1,8,9]. The quantity  $R$  is equated to the sum of inner- and outer-sphere contributions denoted by  $R(in)$  and  $R(out)$ , respectively. One has [8],

$$R(out) = -(\epsilon_{op}^{-1} - \epsilon_s^{-1})e^2/2a, \quad (2)$$

where  $\epsilon_{op}$  and  $\epsilon_s$  are the optical and static dielectric constants of water, respectively, and  $a$  is the radius of the boundary between inner- and outer-sphere regions. Equation (2) yields approximate results, but this does not matter for our purpose because of the large difference between normal and anomalous values of  $R$ . It is not necessary for the same reason to calculate  $R(in)$  in most cases. Equation (2) is applied in sec. 3, and another method for identifying anomalous values of  $R$  is discussed in sec. 4.

### 3. Cyanometalate complexes

Some cyanometalate complexes undergo autoionization. Thus,  $Fe(CN)_6^{4-}$  exhibits two distinct emission bands [10], and the values of  $|R|$  for the complexes of Table 1 are anomalously low except for the second bands of  $Mn(CN)_6^{4-}$  and  $Fe(CN)_6^{4-}$ . In fact,  $|R|$  is amazingly low (0.3 eV) for  $W(CN)_8^{4-}$ , for instance. The threshold energies in Table 1 were determined from the emission spectra in [11] by application of the extrapolation method used in [6,7] and reviewed in [5]. Data on  $\Delta G$  are from [12]. One has a  $\approx 0.45$  nm [13] for the complexes of Table 1. The corresponding free energy,  $R(out) \approx -0.9$  eV, computed from (2) is higher in absolute value than the experimental values of  $|R|$ , except for the second bands of  $Mn(CN)_6^{4-}$  and  $Fe(CN)_6^{4-}$ . The discrepancy is even greater because  $R(in)$  ( $= -0.38$  eV for  $Fe(CN)_6^{4-}$  [13]) should be taken into account and eq. (2) yields somewhat low values of  $|R(out)|$  [14]. Thus, only the second bands of  $Mn(CN)_6^{4-}$  and  $Fe(CN)_6^{4-}$  correspond to normal values of  $R$  and are assigned, on that basis, to direct transitions to the continuum. The assignment of the second band of  $Fe(CN)_6^{4-}$  to autoionization in [10] therefore must be revised.

Autoionization occurs in the range of photon energies in which intense absorption bands are observed [15,16], as required by the analysis of sec. 1. The threshold energies of the autoionization bands of  $Mn(CN)_6^{4-}$  (4.8 eV)



and  $\text{Fe}(\text{CN})_6^{4-}$  (5.5 eV) are slightly lower than the photon energies  $E^{\text{max}} = 4.90$  and  $5.69$  eV [15], respectively, of broad, intense ( $\epsilon^{\text{max}} = 31,100$  and  $24,200 \text{ M}^{-1} \text{ cm}^{-1}$ ) charge transfer absorption bands of these complexes. The complexes  $\text{W}(\text{CN})_8^{4-}$  and  $\text{Mo}(\text{CN})_8^{4-}$  exhibit intense charge transfer bands [16] at  $4.98$  eV ( $\epsilon^{\text{max}} = 25,060 \text{ M}^{-1} \text{ cm}^{-1}$ ) and  $5.17$  eV ( $\epsilon^{\text{max}} = 15,540 \text{ M}^{-1} \text{ cm}^{-1}$ ), respectively. These values of  $E^{\text{max}}$  are lower than the corresponding threshold energies (by  $0.4$  eV) and the sums  $\Delta G_{\text{H}} + \Delta G$  of (1) (by ca.  $0.1$  eV). This is surprising, and it is possible that these complexes exhibit another absorption band at higher photon energies than the preceding  $E^{\text{max}}$  values. It is also possible that the  $E^{\text{max}}$  energies are too low by a few tenths of electronvolt because of the uncertainty in the resolution of the absorption spectrum by superposed multiple Gaussians.

The two emission bands of  $\text{Mn}(\text{CN})_6^{4-}$  in [11] are not as well resolved as for  $\text{Fe}(\text{CN})_6^{4-}$  [10], but they are still apparent. The second band of  $\text{Mn}(\text{CN})_6^{4-}$  has a threshold energy of ca.  $6$  eV and a normal value  $R \approx -1.7$  eV. More exact analysis is not feasible because of the possibility of spurious emission by  $\text{Mn}(\text{CN})_6^{3-}$  for the easily oxidized (by air) solutions of  $\text{Mn}(\text{CN})_6^{4-}$ . The emission spectra of the other complexes of Table 1 were not investigated in [11] at sufficiently high photon energies (up to ca.  $8$  eV) to allow the detection of their normal emission bands by the extrapolation method of sec. 4.

#### 4. Inorganic anions and cations

Definite evidence for autoionization was found for  $\text{NO}_3^-$  and  $\text{ClO}_4^-$  among the common inorganic anions investigated in [17]. The reorganization free energy of  $\text{NO}_3^-$  in aqueous solution is anomalously low in absolute value:  $E^{\text{t}} = 7.46$  eV [17],  $\Delta G = 2.3 \pm 0.1$  eV [18],  $R \approx -0.7$  eV from (1). A second emission band therefore is expected at photon energies corresponding to the

normal value of  $R$ . The plot of the emission yield  $Y$  to the power 0.5 against photon energy (sec. 2, [5]) does exhibit a break at ca. 9.2 eV for the data obtained in [17]. The threshold energies from the two linear segments (7.9 to 9.1 eV and 9.3 to 10.3 eV) of the extrapolation plot are 7.66 and 8.38 eV, respectively. Extrapolation from a plot of  $Y^{0.4}$  rather than  $Y^{0.5}$  generally yields better fits for  $E^t < 8$  eV [6,7,17] (cf. discussion in [5]). The resulting first threshold energy is 7.47 eV in good agreement with  $E^t = 7.46$  eV in [17]. The value  $R = -1.6$  eV computed from (1) for  $E^t = 8.38$  eV is normal in contrast with the anomalous value,  $R = -0.7$  eV, for the autoionization band. It should be noted that extrapolation plots of  $Y^{0.4}$  or  $Y^{0.5}$  against photon energy can yield only an approximate threshold energy of the autoionization band. These plots presuppose a constant product of the emission cross section by the attenuation length of the electron wave in the liquid (cf. discussion in [5]). This can hardly be the case for autoionization bands which have the Gaussian-like shape of absorption bands [4,10].

The change of free energy  $\Delta G$  is not available for application of (1) to emission by  $\text{ClO}_4^-$ . The reorganization free energy  $R$  can be computed in that case from,

$$E^t = A - \Delta G^S - R, \quad (3)$$

where  $A$  is the electron affinity of the  $\text{ClO}_4^-$  radical and  $\Delta G^S$  the free energy of solvation of  $\text{ClO}_4^-$ . Equation (3) involves minor approximations which are stated in its derivation in [5]. One computes  $\Delta G^S = -2.25$  eV for  $\text{ClO}_4^-$  from data in [19,20]. One has:  $E^t = 8.45$  eV for  $\text{ClO}_4^-$  [17],  $A = 5.82$  eV [21], and the anomalous value  $R = -0.38$  eV. Thus, the band at  $E^t = 8.45$  eV is assigned to autoionization. The validity of this assignment rests, of course, on the corrections of the numerical value of  $A$ . A normal value of  $R$  would require  $A$  to be lower by ca. 1 eV than the value used here.

The cations  $\text{Ag}^+$  and  $\text{Tl}^+$  among those studied in [6] have anomalous reorganization free energies:  $E^t = 7.52$  eV,  $\Delta G = 2.0$  eV [12],  $R \approx -1.0$  eV for  $\text{Ag}^+$ ;  $E^t = 7.40$  eV,  $\Delta G = 2.2$  eV [22],  $R \approx -0.7$  eV for  $\text{Tl}^+$ . The anomalous character of these values of  $R$  can be ascertained from the ratio  $\rho = z^2 R / \Delta G^S$ , where  $\Delta G^S$  is the free energy of solvation of the ion having the ionic charge  $z^+$  or  $z^-$ . A numerical value of  $\rho$  is obtained from (2) and the Born equation for  $\Delta G^S$  by neglecting the inner-sphere contribution to  $R$ . Thus,

$$\rho \sim (\epsilon_{\text{op}}^{-1} - \epsilon_s^{-1}) / (1 - \epsilon_s^{-1}). \quad (4)$$

The term  $z^2$  appears in the ratio  $z^2 R / \Delta G^S$  because  $\Delta G^S$  is proportional to  $z^2$  according to the Born equation whereas  $R(\text{out})$  of (2) is independent of  $z$ . Equation (3) is based on a crude model but it yields the value,  $\rho = 0.56$ , for aqueous solutions at room temperature in fair agreement with experiment (Table 2), namely  $0.42 \leq z^2 R / \Delta G^S \leq 0.53$ . It should be noted that the values of  $\Delta G^S$  used in the calculation of  $\rho$  and the quantity  $\Delta G_H$  in (1) are not independent, as one can ascertain from appropriate thermodynamic cycles. The value of  $\rho$  therefore depends somewhat on the choice of the numerical value of  $\Delta G_H$  in (1). This dependence is not significant for our present purpose because the values of  $\rho$  for  $\text{Ag}^+$  ( $\rho = 1.0/4.96 = 0.20$ ) and  $\text{Tl}^+$  ( $\rho = 0.7/3.56 = 0.20$ ) are clearly too low ( $\Delta G^S$  values from [23]).

Reexamination of the results in [6] for TlF yielded a  $\gamma^{0.5}$  extrapolation plot (from 9.2 to 10.3 eV) and  $E^t = 8.26$  eV for the normal emission band of  $\text{Tl}^+$ . The corresponding value  $R \approx -1.6$  eV computed for  $\Delta G = 2.2$  eV [22] is normal whereas the value  $R \approx -0.7$  eV for the autoionization band is anomalous. The threshold energy for the second band of  $\text{Ag}^+$  could not be determined because of emission by the anion ( $\text{ClO}_4^-$ ,  $E^t = 8.45$  eV [17]) in the range of photon energies in which this band occurs and is expected.

### 5. Correlation with thermal electron transfer

The activation free energy  $\Delta G_X^\ddagger$  for thermal electron transfer in solution can be correlated [14] to the reorganization free energy  $R$  for emission on the basis of the theories [1] of Marcus [8] and Hush [9]. One has  $\Delta G_X^\ddagger = w + R_X/4$  in the case in which the change of free energy is equal to zero (isotope labeling). There,  $w$  is the work required to bring the two reactants from infinity in solution to the activated complex, and  $R_X$  is the reorganization free energy for thermal electron exchange. The latter is [14]  $R_X \sim R + R(\text{in})$ , where  $R$  has its normal value.

Unwitting use of anomalous values of  $R$  leads to  $\Delta G_X^\ddagger$ 's which are too low. This was the case in [14] for  $\text{Fe}(\text{CN})_6^{4-}$ . Using  $R = -0.6$  eV (Table 1),  $R(\text{in}) = -0.38$  eV [13],  $w = 0.04$  eV [14], one computes  $\Delta G_X^\ddagger = 0.29$  eV against 0.47 eV from experiment. The value  $\Delta G_X^\ddagger = 0.56$  eV computed from the normal value  $R = -1.7$  eV is closer to the experimental result.

### Acknowledgment

This work was supported by the Office of Naval Research and the National Science Foundation. Mr. A. Dziedzic did the computer treatment of the data on  $\text{NO}_3^-$  and  $\text{Tl}^+$ .

### References

- [1] R. D. Cannon, Electron transfer reactions (Butterworths, London, 1980), pp. 175-222, 267-297.
- [2] R. A. Marcus, Ann. Rev. Phys. Chem. 15 (1964) 155.
- [3] G. Herzberg, Molecular spectra and molecular structure, vol. III (Van Nostrand, Princeton, 1966), p. 455.
- [4] H. Aulich, P. Delahay, and L. Nemec, J. Chem. Phys. 59 (1973) 2354.
- [5] P. Delahay, Acc. Chem. Res. 15 (1982) 40.

- [6] P. Delahay, K. von Burg, and A. Dziedzic, Chem. Phys. Letters 79 (1981) 157.
- [7] P. Delahay and K. von Burg, Chem. Phys. Letters 83 (1981) 250.
- [8] R. A. Marcus, J. Chem. Phys. 24 (1956) 966; 43 (1965) 679.
- [9] N. S. Hush, Trans. Faraday Soc. 57 (1961) 557.
- [10] L. Nemec, L. Chia, and P. Delahay, J. Phys. Chem. 79 (1975) 2935.
- [11] L. Nemec and P. Delahay, J. Chem. Phys. 57 (1972) 2135.
- [12] W. M. Latimer, Oxidation potentials, 2nd ed. (Prentice-Hall, New York, 1952).
- [13] J. M. Hale in Reactions of molecules at electrodes, N. S. Hush, ed. (Wiley-Interscience, New York, 1971), pp. 229-257.
- [14] P. Delahay, Chem. Phys. Letters 87 (1982) 607.
- [15] J. J. Alexander and H. Gray, Coord. Chem. Rev. 2 (1967) 29.
- [16] J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, J. Am. Chem. Soc. 85 (1963) 249.
- [17] K. von Burg and P. Delahay, Chem. Phys. Letters 78 (1981) 287.
- [18] V. M. Berdnikov and N. M. Bazhin, Russ. J. Phys. Chem. 44 (1970) 395.
- [19] H. F. Halliwell and S. C. Nyburg, Trans. Faraday Soc. 59 (1963) 1126.
- [20] H. L. Friedman and C. V. Krishnan in Water, vol. 3, F. Franks, ed. (Plenum Press, New York, 1973), pp. 1-118.
- [21] L. G. Christophorou, Atomic and molecular radiation physics (Wiley-Interscience, New York, 1971), p. 566.
- [22] B. Falcinella, P. D. Felgate, and G. S. Laurence, J. Chem. Soc. Dalton (1974) 1367.
- [23] R. M. Noyes, J. Am. Chem. Soc. 84 (1962) 513.

Table 1

Data on cyanometalate complexes

	$E^t$ a) (eV)	$\Delta G$ b) (eV)	$-R$ (eV)
$Mn(CN)_6^{4-}$	ca. 4.8	-0.22	ca. 0.5
	ca. 6		ca. 1.7
$Fe(CN)_6^{4-}$	5.5	0.36	0.6
	ca. 6.6		ca. 1.7
$Fe(CN)_5NH_3^{3-}$	5.4	0.37	0.5
$Fe(CN)_5H_2O^{3-}$	5.4	0.49	0.4
$W(CN)_8^{4-}$	5.4	0.57	0.3
$Mo(CN)_8^{4-}$	5.6	0.73	0.4

a) Extrapolation plots prepared from data in [11].  $E^t = 6.6$  eV for  $Fe(CN)_6^{4-}$  from 1.1 eV interval between emission bands in [10].

b) From [12].

Table 2

Correlation between reorganization and solvation free energies

	$E^t$ a) (eV)	$\Delta G$ b) (eV)	$-R$ (eV)	$-\Delta G^s$ c) (eV)	$z^2 R / \Delta G^s$
$OH^-$	8.45	1.9	2.05	4.2	0.49
$Cl^-$	8.81	2.55	1.76	3.30	0.53
$Br^-$	8.05	2.0	1.55	3.00	0.52
$I^-$	7.19	1.4	1.29	2.61	0.49
$V^{2+}$	6.38	-0.25	2.13	19.12	0.45
$Cr^{2+}$	6.14	-0.41	2.05	19.28	0.43
$Mn^{2+}$	8.08	1.56	2.02	18.92	0.43
$Fe^{2+}$	7.95	0.77	2.08	19.58	0.42
$Co^{2+}$	8.60	1.84	2.26	20.85	0.43

a) From [6,7].

b) From [12,18].

c) From [23] except for  $OH^-$  [7].

## Captions to Figures

Fig. 1. Potential energy against generalized coordinate for nuclear configuration in the cases of direct optical transition to the continuum (left) and autoionization (right).

Fig. 2. Plots of the emission yield  $Y$  to the powers 0.4 (top) and 0.5 (bottom) against photon energy for 1 M  $\text{NaNO}_3$  (data from [17]).



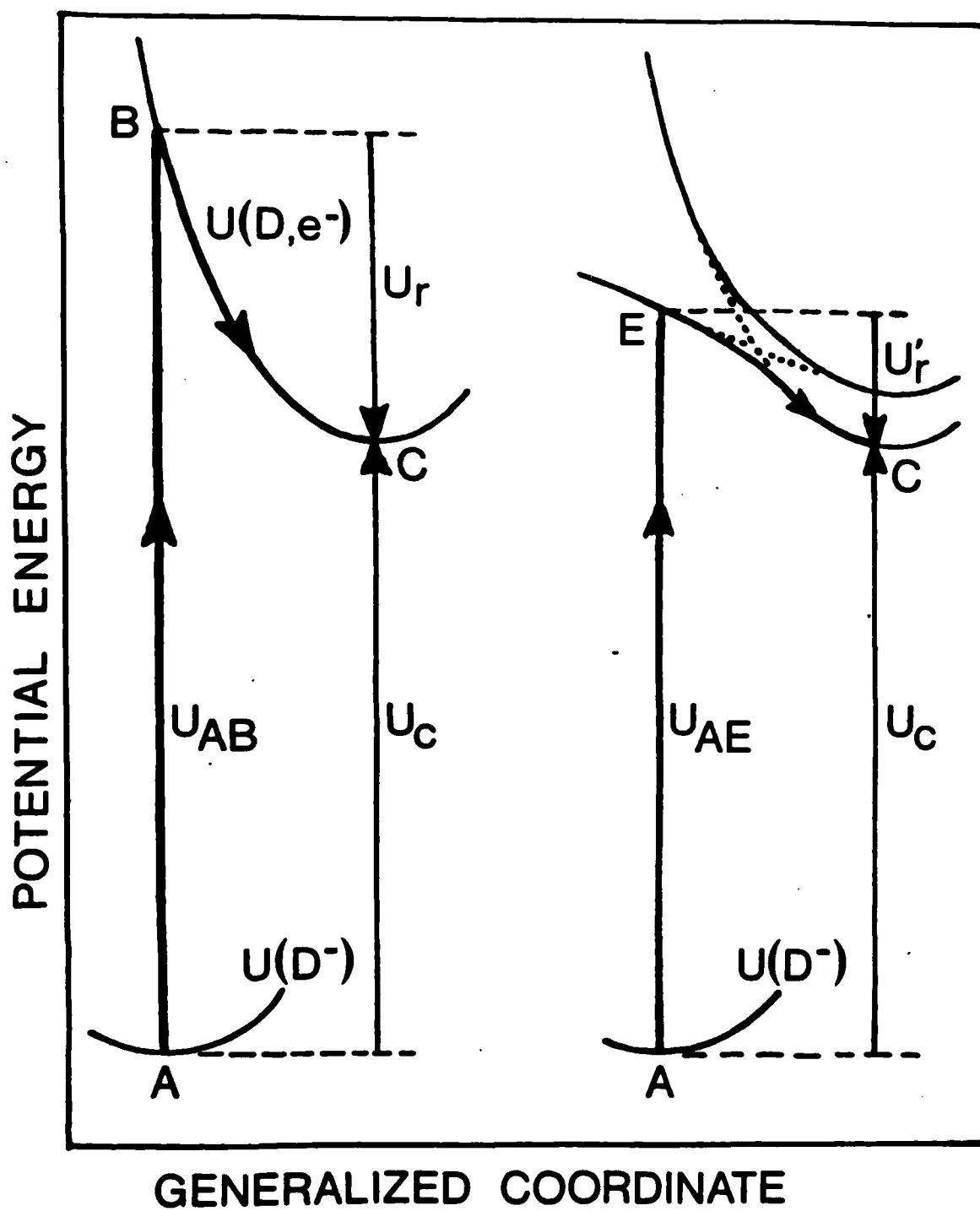


FIG. 1

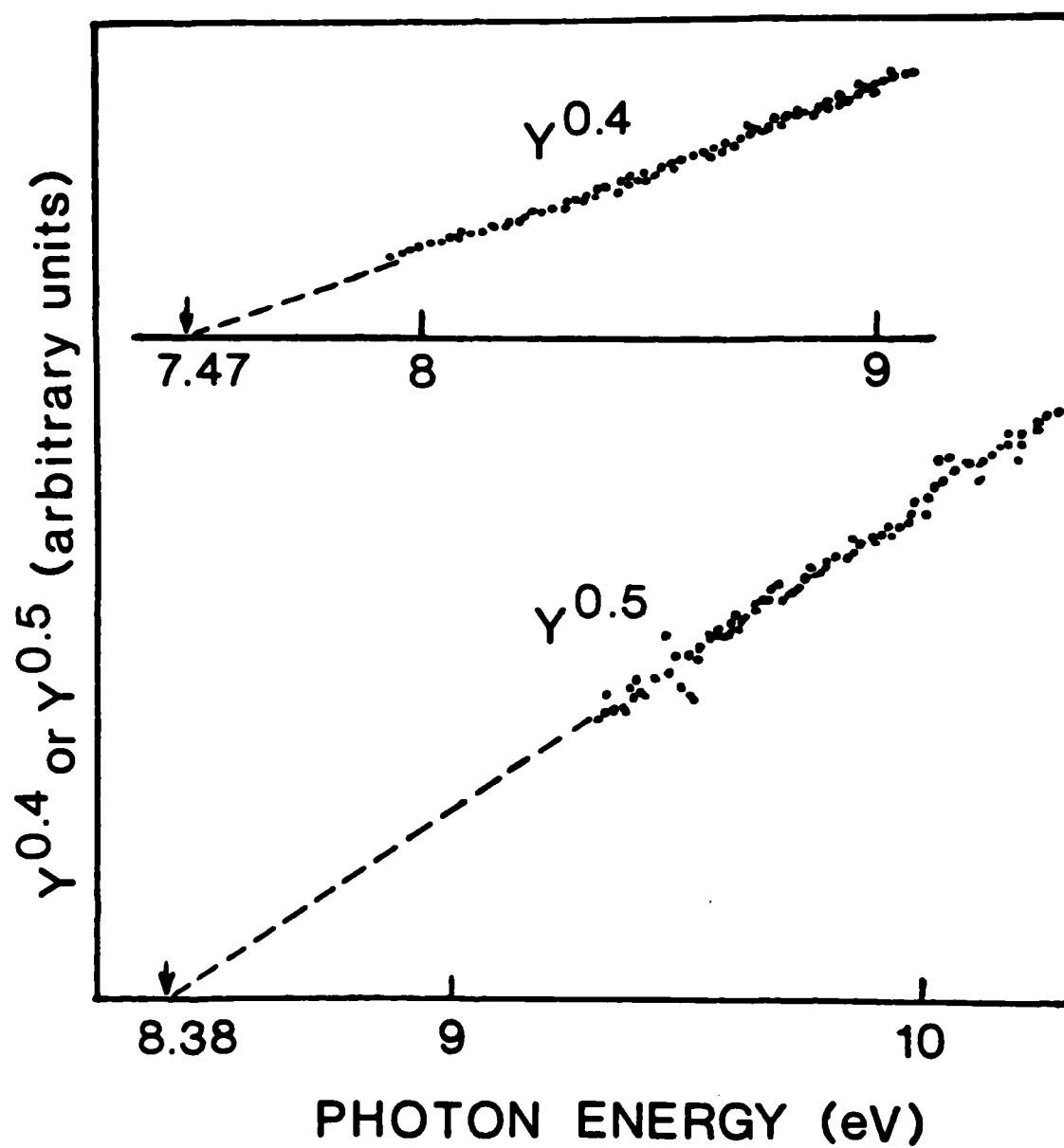


FIG. 2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Western Regional Office Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Eastern Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Naval Weapons Center Attn: Dr. A. B. Amster, Chemistry Division China Lake, California 93555	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
		Mr. & John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1

TECHNICAL REPORT DISTRIBUTION LIST, GENNo.  
Copies

Mr. James Kelley  
DTNSRDC Code 2803  
Annapolis, Maryland 21402

1

Mr. A. M. Anzalone  
Administrative Librarian  
PLASTEC/ARRADCOM  
Bldg 3401  
Dover, New Jersey 07801

1

TECHNICAL REPORT DISTRIBUTION LIST, OSIS

	<u>No. Copies</u>		<u>No. Copies</u>
Professor K. Wilson Department of Chemistry, B-014 University of California, San Diego La Jolla, California 92093	1	Dr. B. Vonnegut State University of New York Earth Sciences Building 1400 Washington Avenue Albany, New York 12203	1
Professor C. A. Angell Department of Chemistry Purdue University West Lafayette, Indiana 47907	1	Dr. Hank Loos Laguna Research Laboratory 21421 Stans Lane Laguna Beach, California 92651	1
Professor P. Meijer Department of Physics Catholic University of America Washington, D.C. 20064	1	Dr. John Latham University of Manchester Institute of Science & Technology P.O. Box 88 Manchester, England M601QD	1
Dr. S. Greer Chemistry Department University of Maryland College Park, Maryland 20742	1		
<del>Professor P. Delachy</del> New York University 100 Washington Square East New York, New York 10003	1		
Dr. T. Ashworth Department of Physics South Dakota School of Mines & Technology Rapid City, South Dakota 57701	1		
Dr. G. Gross New Mexico Institute of Mining & Technology Socorro, New Mexico 87801	1		
Dr. J. Kassner Space Science Research Center University of Missouri - Rolla Rolla, Missouri 65401	1		
Dr. J. Telford University of Nevada System Desert Research Institute Lab of Atmospheric Physics Reno, Nevada 89507	1		

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. Paul Delahay Department of Chemistry New York University New York, New York 10003	1	Dr. P. J. Hendra Department of Chemistry University of Southampton Southampton SO9 5NH United Kingdom	1
Dr. E. Yeager Department of Chemistry Case Western Reserve University Cleveland, Ohio 44106	1	Dr. Sam Perone Department of Chemistry Purdue University West Lafayette, Indiana 47907	1
Dr. D. N. Bennion Department of Chemical Engineering Brigham Young University Provo, Utah 84602	1	Dr. Royce W. Murray Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514	1
Dr. R. A. Marcus Department of Chemistry California Institute of Technology Pasadena, California 91125	1	Naval Ocean Systems Center Attn: Technical Library San Diego, California 92152	1
Dr. J. J. Auburn Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. C. E. Mueller The Electrochemistry Branch Materials Division, Research & Technology Department Naval Surface Weapons Center White Oak Laboratory Silver Spring, Maryland 20910	1
Dr. Adam Heller Bell Laboratories Murray Hill, New Jersey 07974	1	Dr. G. Goodman Globe-Union Incorporated 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. T. Katan Lockheed Missiles & Space Co, Inc. P.O. Box 504 Sunnyvale, California 94088	1	Dr. J. Boechler Electrochimica Corporation Attention: Technical Library 2485 Charleston Road Mountain View, California 94040	1
Dr. Joseph Singer, Code 302-1 NASA-Lewis 21000 Brookpark Road Cleveland, Ohio 44135	1	Dr. P. P. Schmidt Department of Chemistry Oakland University Rochester, Michigan 48063	1
Dr. B. Brummer EIC Incorporated 55 Chapel Street Newton, Massachusetts 02158	1	Dr. F. Richtol Chemistry Department Rensselaer Polytechnic Institute Troy, New York 12181	1
Library P. R. Mallory and Company, Inc. Northwest Industrial Park Burlington, Massachusetts 01803	1		

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. A. B. Ellis Chemistry Department University of Wisconsin Madison, Wisconsin 53706	1	Dr. R. P. Van Duyne Department of Chemistry Northwestern University Evanston, Illinois 60201	1
Dr. M. Wrighton Chemistry Department Massachusetts Institute of Technology Cambridge, Massachusetts 02139	1	Dr. B. Stanley Pons Department of Chemistry University of Alberta Edmonton, Alberta CANADA T6G 2G2	1
Larry E. Flew Naval Weapons Support Center Code 30736, Building 2906 Crane, Indiana 47522	1	Dr. Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824	1
S. Rubv DOE (STOR) 600 E Street Washington, D.C. 20545	1	Dr. R. David Rauh EIC Corporation 55 Chapel Street Newton, Massachusetts 02158	1
Dr. Aaron Wold Brown University Department of Chemistry Providence, Rhode Island 02192	1	Dr. J. David Margerum Research Laboratories Division Hughes Aircraft Company 3011 Malibu Canyon Road Malibu, California 90265	1
Dr. R. C. Chudacek McGraw-Edison Company Edison Battery Division Post Office Box 28 Bloomfield, New Jersey 07003	1	Dr. Martin Fleischmann Department of Chemistry University of Southampton Southampton 509 5NH England	1
Dr. A. J. Bard University of Texas Department of Chemistry Austin, Texas 78712	1	Dr. Janet Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. M. M. Nicholson Electronics Research Center Rockwell International 3370 Miraloma Avenue Anaheim, California	1	Dr. R. A. Osteryoung Department of Chemistry State University of New York at Buffalo Buffalo, New York 14214	1
Dr. Donald W. Ernst Naval Surface Weapons Center Code R-33 White Oak Laboratory Silver Spring, Maryland 20910	1	Mr. James R. Moden Naval Underwater Systems Center Code 3632 Newport, Rhode Island 02840	1

TECHNICAL REPORT DISTRIBUTION LIST, 359

	<u>No. Copies</u>		<u>No. Copies</u>
Dr. R. Nowak Naval Research Laboratory Code 6130 Washington, D.C. 20375	1	Dr. Bernard Spielvogel U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709	1
Dr. John F. Houlihan Shenango Valley Campus Pennsylvania State University Sharon, Pennsylvania 16146	1	Dr. Denton Elliott Air Force Office of Scientific Research Bolling AFB Washington, DC 20332	1
Dr. D. F. Shriver Department of Chemistry Northwestern University Evanston, Illinois 60201	1	Dr. David Aikens Chemistry Department Rensselaer Polytechnic Institute Troy, NY 12181	1
Dr. D. H. Whitmore Department of Materials Science Northwestern University Evanston, Illinois 60201	1	Dr. A. P. B. Lever Chemistry Department York University Downsview, Ontario M3J1P3 Canada	1
Dr. Alan Bewick Department of Chemistry The University Southampton, SO9 5NH England	1	Mr. Maurice F. Murphy Naval Sea Systems Command 63R32 2221 Jefferson Davis Highway Arlington, VA 20360	1
Dr. A. Hiny NAVSEA-5433 NC #4 2541 Jefferson Davis Highway Arlington, Virginia 20362	1	Dr. Stanislaw Szpak Naval Ocean Systems Center Code 6343 San Diego, CA 95152	1
Dr. John Kincaid Department of the Navy Strategic Systems Project Office Room 901 Washington, DC 20376	1	Dr. Gregory Farrington Department of Materials Science & Engineering University of Pennsylvania Philadelphia, PA 19104	1
M. L. Robertson Manager, Electrochemical Power Sonics Division Naval Weapons Support Center Crane, Indiana 47522	1	Dr. Bruce Dunn Department of Engineering & Applied Science University of California Los Angeles, CA 90024	1
Dr. Elton Cairns Energy & Environment Division Lawrence Berkeley Laboratory University of California Berkeley, California 94720	1		



TECHNICAL REPORT DISTRIBUTION LIST, 359No.  
Copies

Dr. Micha Tomkiewicz  
Department of Physics  
Brooklyn College  
Brooklyn, NY 11210

1

Dr. Lesser Blum  
Department of Physics  
University of Puerto Rico  
Rio Piedras, PR 00931

1

Dr. Joseph Gordon II  
IBM Corporation  
K33/281  
5600 Cottle Road  
San Jose, CA 95193

1

Dr. Robert Somoano  
Jet Propulsion Laboratory  
California Institute of Technology  
Pasadena, CA 91103

1

**FILMED**

**09-8**